A DEGRADATION STUDY FOR DISLODGEABLE METHAMIDOPHOS (MONITOR) RESIDUE ON BROCCOLI AND BRUSSELS SPROUTS FOLIAGE IN MONTEREY COUNTY, CALIFORNIA

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SUMMARY

Three fields (2 broccoli and 1 brussels sprouts) in Monterey County, were sampled for dislodgeable foliar pesticide residue after application of methamidophos (Monitor). Samples were collected before the application; immediately after application at 12, 24, 48 and 72 hours; and, at 7 days post-application. As an interim measure (until data gaps are filled) a residue level of 0.66 ug/cm^2 has been set as a level at which unprotected field workers could reenter a field with little hazard. For the two broccoli fields, this level was reached between the 12 hour and 48 hour samples. On the Brussels sprouts, residues were never above the safe level.

INTRODUCTION

Methamidophos (O,S-dimethyl phosphoramidothioate, Monitor) is a Toxicity Category I organophosphate insecticide used extensively in agriculture. Monitor has an oral LD_{50} (rat) of 7.5 mg/kg and an acute dermal LD_{50} (rat) of 50 mg/kg (NIOSH, 1979). The most common adverse effect of organophosphate poisoning is cholinesterase inhibition, which may lead to such symptoms as nausea, vomiting, dizziness, etc.

In June 1971, the California Department of Food and Agriculture established reentry intervals for specific crop/pesticide combinations (California, 1982). A reentry interval is the time period that must elapse between the application of a pesticide and the entry of unprotected workers into a treated area. This waiting period was instituted to allow sufficient time for toxic materials to environmentally degrade to a low-toxicity residue level. The adequacy of these safety intervals has not been completely evaluated since their introduction. This study was initiated to validate the existing reentry interval for Monitor. The objective of this study was to monitor the foliar decay rate and determine when worker reentry may occur. This study is one of several studies conducted for reentry interval validation.

METHODS AND MATERIALS

With the assistance of the Monterey County Agricultural Commissioner's Office, cooperation was obtained from growers and pest control operators (PCOs) who would be using Monitor. The material used was Ortho Monitor 4 Spray, EPA Reg. No. 239-2404 AA, registered by Chevron Chemical Company. The material contains 40% active ingredient with a maximum application rate of 2 pints of formulated material per acre. The application rate used in these studies was 2 pints of Ortho Monitor 4 Spray (1 pound active ingredient) per acre. The dilution rate was 100 gallons of water per acre for the Brussels sprouts, and 15 gallons of water per acre for the broccoli.

The reentry interval for the broccoli fields was two days and three days for the Brussels sprouts field (other organophosphates were applied with Monitor). The applications to broccoli were delivered by aerial aircraft. The tank mix also contained Pydrin, Bravo 500, Dithane M-22, and Nufilm P. The application to the Brussels sprouts field was delivered by ground equipment. This tank mix also contained Phosdrin 4, Systox-2, Ambush WP, and Bravo 500. The broccoli fields were 29.2 acres and 52.8 acres. The Brussels sprouts field was 11.7 acres.

The selected sampling area in each field was divided into three areas. Non-adjacent rows from each of these areas were chosen as the sample rows. These rows were designated A, B, and C. Each sample consisted of a composite of leaf punches from each of the three rows. Each sampled row was marked at the beginning of the row and at the locations of the first plant and last plant sampled in that row. In Row A, sampling began on the plant 25 meters from the edge of the field. In Row B, sampling started near the middle of the row; and in Row C, sampling began such that the turn-around point on that sampling row was 25 meters from the opposite end. This layout approximated a diagonal across the sampling area. Sixteen leaf punches (each 2.54 sq. cm. in diameter) were taken from each row; eight on the right entering the row, and eight on the left exiting the row. Punches were taken

from leaves presenting the greatest exposed surface area. Three replicate samples were obtained simultaneously at each sampling interval. Each sample contained 48 leaf discs accumulated in a four ounce glass jar. The leaf punch was cleaned with alcohol between row samplings. Sample jars were sealed with aluminum foil, capped, and stored on wet ice. The ice was constantly replenished to insure temperature stability. All required protective equipment was worn during sampling.

Samples were collected prior to the application. Post-application samples were taken within two hours after the application and at 12 hours, 24 hours, 48 hours, 72 hours, and 7 days.

Samples were shipped to Chemistry Laboratory Services in Sacramento for analysis. The procedure for gas chromatography (GC) analysis of Monitor is given in Appendix I. The minimal detectable level for Monitor is 0.001 ug/cm^2. Weather conditions were clear and sunny with no rain-fall. The high temperatures ranged from approximately 61° to 78°F with lows ranging from 41° to 55°F.

RESULTS

The results for Monitor residue analysis are given in Table 1. The dislodgeable residue decay rates are illustrated in Figure 1. Knaak, et. al. (1980) has calculated "safe levels" of dislodgeable residue for certain pesticides. This is a level of foliar residue in which an unprotected field worker could reenter a treated area with little or no hazard. A safe level has not been calculated for Monitor; but, by comparing dermal LD_{50} values with chemicals that do have calculated safe levels, a safe level can be estimated for Monitor. The safe level that has been calculated for Monitor is 0.66 ug/cm^2 (Maddy, 1985). Residue levels in the broccoli fields fell to this level between the 12 hour and 48 hour samples. This level was never reached after application to the Brussels sprouts field.

In evaluating the reasons for the slower decay on broccoli, we should look at the different application techniques. On the broccoli, the application took place aerially in only 15 gallons of water per acre while the ground application was completed in 100 gallons of water per acre. Work by Carmen, et. al. (1972) with several organophosphates on citrus, suggests that low volume applications result in higher residues on leaf surfaces than more dilute sprays. Studies by Dorough and Randolph (1967) suggest that for total residue there is a higher initial deposition and longer residual action for concentrated sprays.

DISCUSSION

Under the conditions in which this study was conducted, the residue levels did not drop as rapidly as expected. Therefore, at the expirations of the reentry interval for Monitor alone on broccoli (24 hours), workers may be in danger of exposure to excessive residues. Further studies will be necessary to fully substantiate the effects of different environmental and application conditions on the degradation profile.

TABLE 1
MONITOR DEGRADATION DATA
(ug/cm^2)

FIELD 1 - Broccoli

DAY	REP A	REP B	REP C	Average Residue
Pre-Application	N.D.	N.D.	N.D.	N.D.
Immed. Post	1.20	1.20	1.30	1.23
12 Hours Post	0.65	0.48	0.44	0.52
24 Hours Post	0.25	0.24	0.29	0.26
48 Hours Post	0.15	0.13	0.11	0.13
72 Hours Post	0.08	0.15	0.09	0.11
7 Days Post	0.03	0.01	0.03	0.02

FIELD 2 - Broccoli

DAY	REP A	REP B	REP C	Average Residue
Pre-Application	N.D.	N.D.	N.D.	N.D.
Immed. Post	2.40	1.60	2.00	2.00
12 Hours Post	1.00	1.20	1.00	1.07
24 Hours Post	0.85	0.73	0.40	0.66
48 Hours Post	0.22	0.34	0.42	0.33
72 Hours Post	0.19	0.25	0.21	0.22
7 Days Post	0.03	0.03	0.07	0.04

FIELD 3 - Brussels sprouts

DAY	REP A	REP B	REP C	Average Residue
Pre-Application	N.D.	N.D.	N.D.	N.D.
Immed. Post	0.55	0.46	0.69	0.57
12 Hours Post	0.19	0.29	0.21	0.23
24 Hours Post	0.02	0.05	0.03	0.03
48 Hours Post	0.05	0.04	0.02	0.04
7 Days Post	0.02	0.01	0.01	0.01

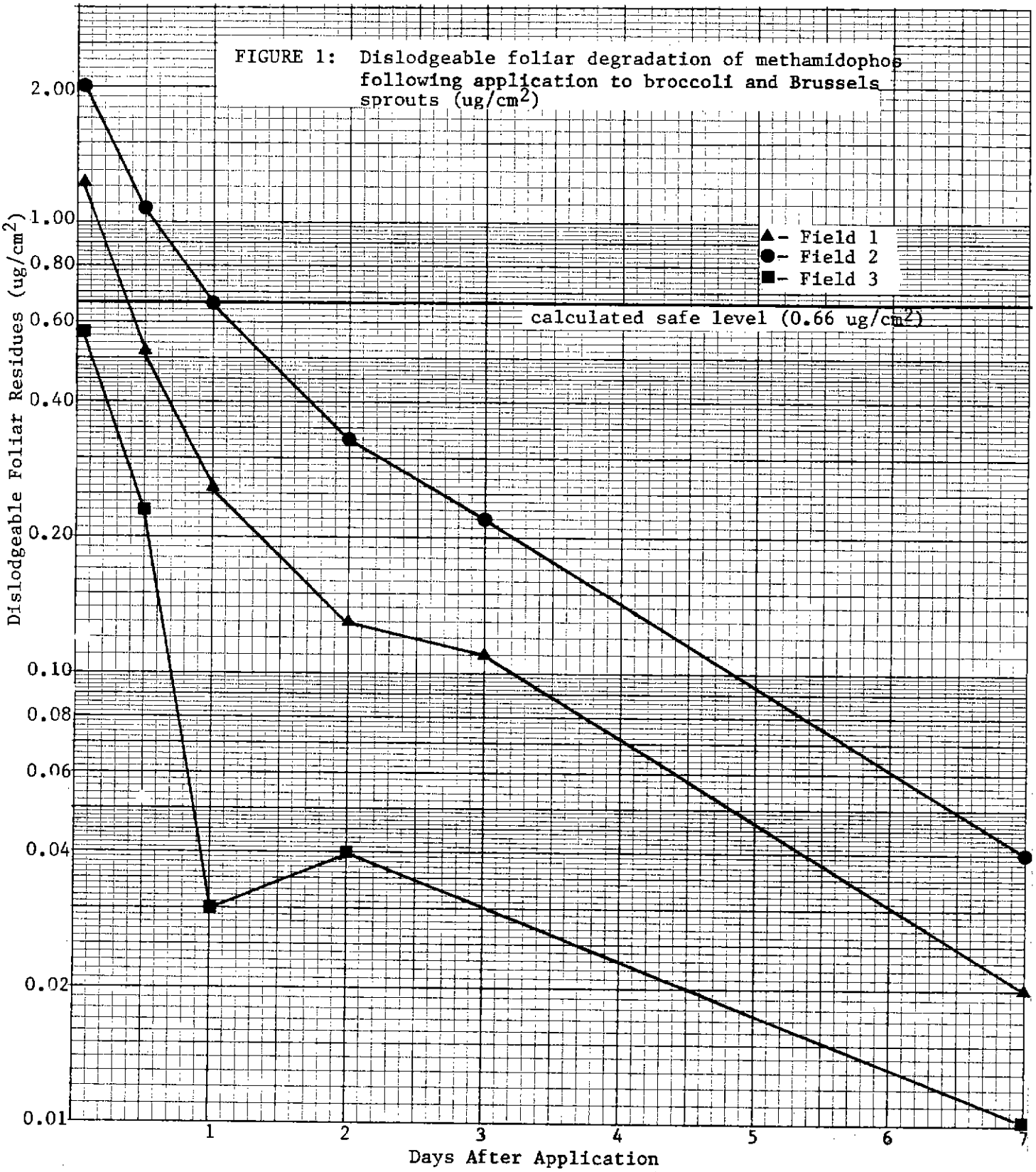
FIGURE 1: Dislodgeable foliar degradation of methamidophos following application to broccoli and Brussels sprouts (ug/cm2)
Dislodgeable Foliar Residues (ug/cm2)
2.00
1.00
0.80
0.60
0.40
0.20
0.10
0.08
0.06
0.04
0.02
0.01
▲– Field 1
●– Field 2
■– Field 3
calculated safe level (0.66 ug/cm2)
1
2
3
4
5
6
7
Days After Application

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APPENDIX I
ANALYTICAL PROCEDURES FOR THE SCREENING
OF DISLODGEABLE MONITOR RESIDUES

SCOPE:

This method is for the dislodgeable analysis of Monitor from leaf punch surfaces.

PRINCIPLE:

Monitor is stripped from leaf punch surfaces using a water and surfactant solution. The resulting aqueous solution is brought to a known final volume (not to exceed 200 mls) and a 20% aliquot is taken and blended with Ethyl Acetate and Na2SO4. The Ethyl Acetate is evaporated to a desired volume and analyzed by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Distilled water.
2. 2% Sur-ten solution.
3. Ethyle Acetate, nanograde. Check for interferences.
4. Na2SO4, anhydrous.
5. Analytical standard of Monitor:
   a) Stock standard - 1 mg/ml
   b) Working standards - Dilute stock standard to several working standards covering the linear range of the gas chromatograph and the detector used, e.g., .01 to 10 ng/ul.
6. Sorval blender, 500 ml capacity blender cup with blade.
7. Boiling flasks, 500 ml capacity.
8. Stemmed, glass funnels.
9. Volumetric test tubes.
10. Graduated cylinders, 250 ml capacity with glass stoppers.
11. Rotoevaporator.
12. Rotator.
13. Gas Chromatograph equipped with a Nitrogen-Phosphorous detector and capillary injection system.
14. A 25 meter by 0.2 mm I.D. SE-54 coated fused silica capillar column.

ANALYSIS:

1. Add 50 mls of distilled water and 0.2 ml of 2% Sur-ten solution to the jar containing the leaf punches.
2. Rotate the jar for 30 minutes.
3. Decant aqueous solution into a graduated cylinder.
4. Repeat steps 1 through 3 twice more.
5. Bring the final volumn in the graduated cylinder to 150 mls.
6. Take a 20% aliquot (30 mls) and mix with 150 mls of EtAc in a Sorval blender cup.

7. Add 125 grams of Na_2SO_4 to the cup and blend for 2 minutes on high speed.
8. Decant EtAc through Na_2SO_4 into a 500 ml boiling flask.
9. Add an additional 50 mls of EtAc to the blender cup and blend again on high speed for 2 minutes.
10. Decant EtAc into boiling flask containing the first extract and evaporate to 5 mls.
11. Quantitatively transfer with EtAc into a volumetric test tube and bring to a final volumn of 10 mls.
12. Extract is ready for analysis by gas chromatography.

DESORPTION COEFFICIENT:

Recoveries: 10 ug spike - 98%
100 ug spike - 99%

EQUIPMENT CONDITIONS:

1. Gas Chromatograph: HP 5880A
   a) Oven Temperature - 120°C
   b) Injector Temperature - 225°C
   c) Detector Temperature - 250°C
   d) For Capillary Configuration
      i) Column pressure - 15 PSI
      ii) Helium makeup gas flow rate - 25 mls/minute
      iii) Split flow - 50 mls/minute
      iv) Septum purge - 2 mls/minute

CALCULATIONS:

At this time, results are reported in micrograms/cm^2.